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Ultrabroadband, time-resolved THz spectroscopy of disordered materials

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Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

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Ultrabroadband, time-resolved THz spectroscopy of disordered materials

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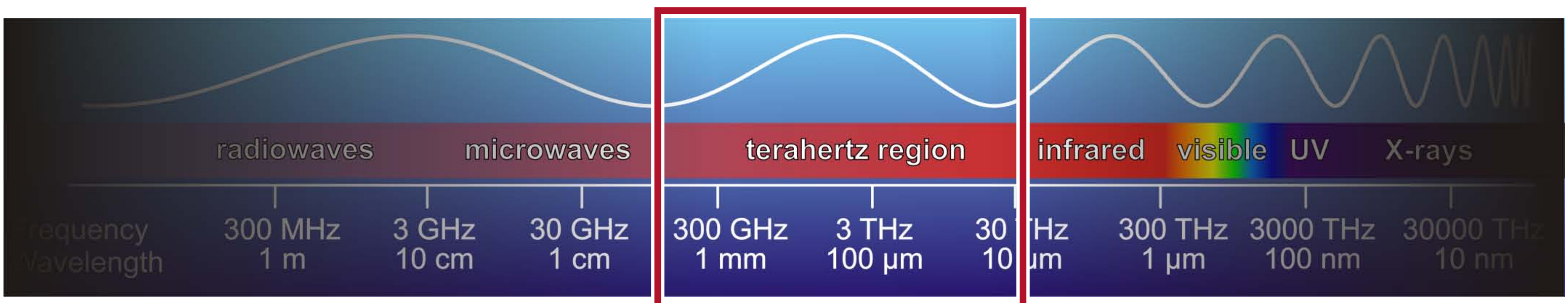
Outline

- Single-cycle, ultrabroadband light at long wavelengths
- Time-resolved THz spectroscopy
- AC conductivity: Drude and non-Drude response
  - Silicon nanoparticles
  - Polymer solar cells
- Adiabatic field compression to MV/cm field strengths



Early prediction of THz technology

…"Get to the point man. W

"Ah me, these excitable, h ed Duval. "What we did was to make a type of low-p waves of very high frequency, it used far in n we were sure no creature could possibly see, how

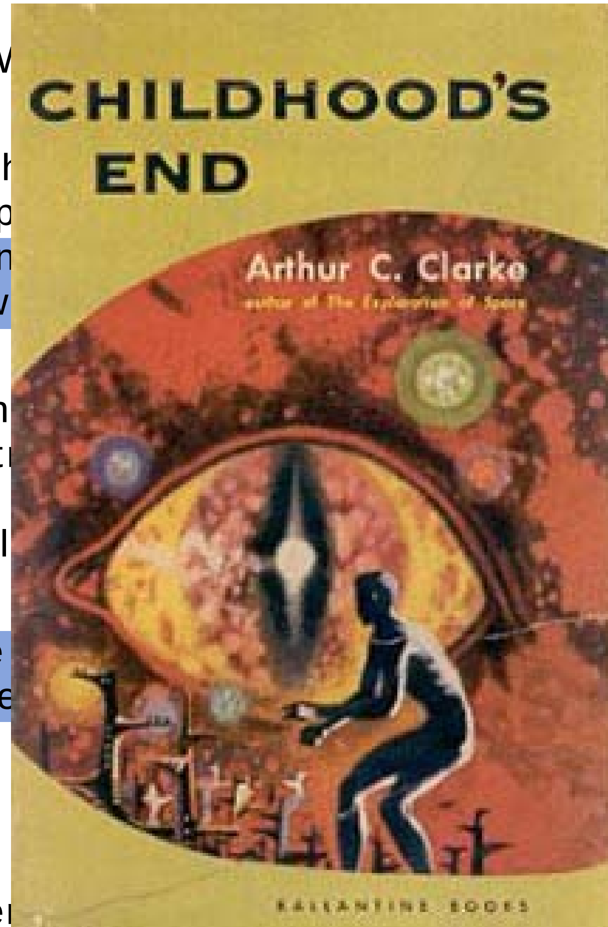
…"We've proved that th screen of yours. The screen is about three centimet s at least ten meters across. We couldn't detect any ardly expected to with the low power which was al did get *this*."

He pushed across a piece was a single wavy line. In one spot was a kink like uake.

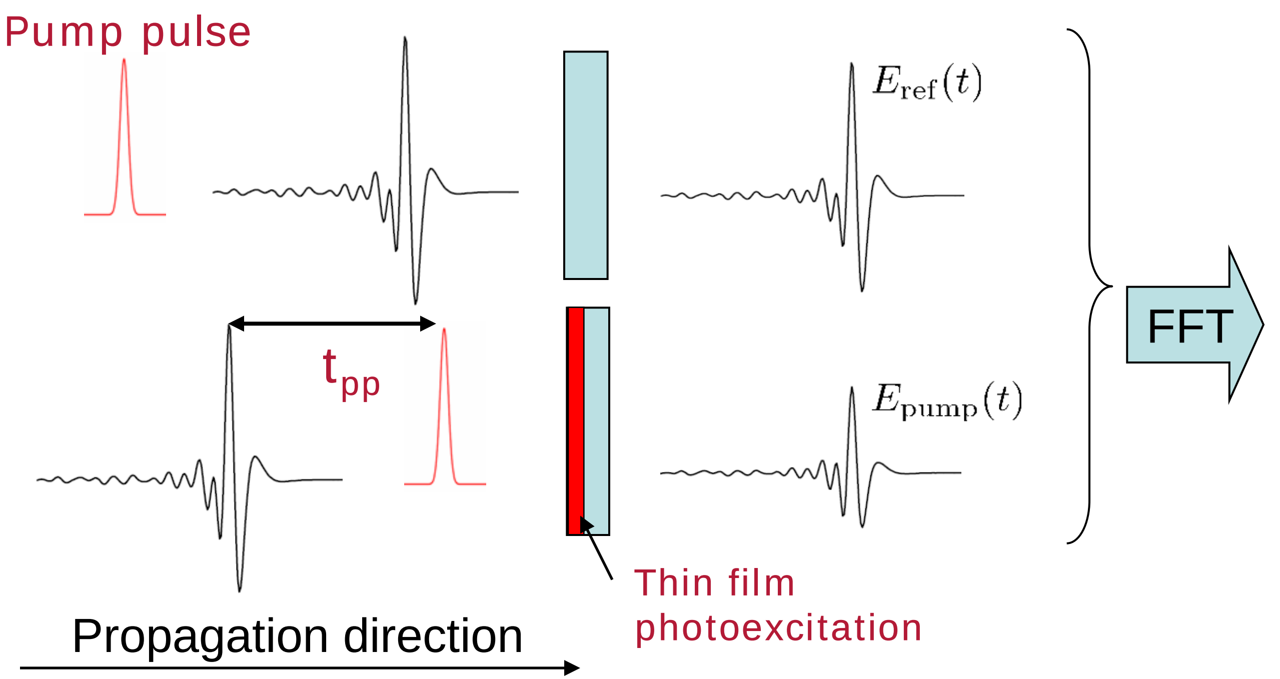
"See that little kink?"

"Yes, what is it?"

"Only Karellen [the alie had been a bit better, we might even have calculated his size."



Time-resolved Terahertz Spectroscopy (TRTS)



$$\frac{\tilde{E}_{\mathrm{pump}}(\omega)}{\tilde{E}_{\mathrm{ref}}(\omega)} = \tilde{T}(\omega)$$

$$\tilde{T}(\omega) = |T(\omega)|e^{i\Phi(\omega)}$$

amplitude

phase

Extraction of spectroscopic data

Transmission amplitude and phase

THz-TDS raw data:

$$E_{ref}(t), E_{pump}(t) \xrightarrow{\text{FFT}} E_{ref}(\omega), E_{pump}(\omega) \longrightarrow \begin{aligned} T(\omega) &= \frac{|E_{pump}(\omega)|}{|E_{ref}(\omega)|} \\ \Theta(\omega) &= \theta_{pump} - \theta_{ref} \end{aligned}$$

Transmission amplitude and phase are then used to calculate optical properties;

$$\hat{n} = n + i\kappa, \quad \hat{\epsilon} = \epsilon' + i\epsilon'', \quad \Delta\hat{\sigma} = \Delta\sigma' + i\Delta\sigma''$$

Photoexcited charge carriers in semiconductors are best described by their conductivity:

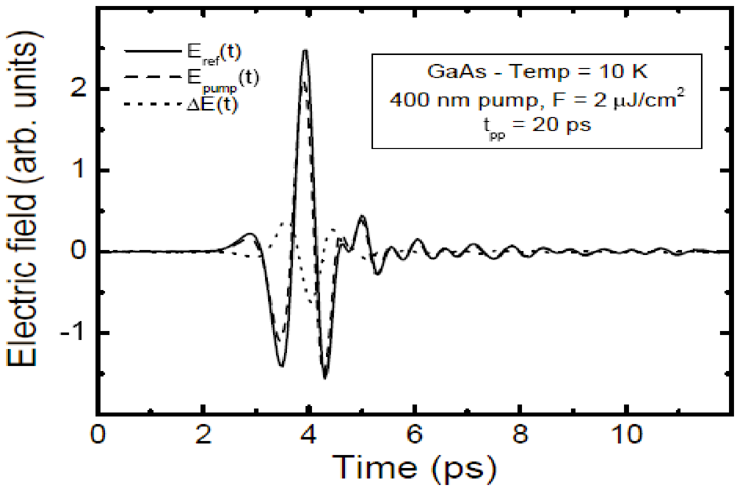
$$\Delta\sigma_s'(\omega) = \frac{N+1}{Z_0}\left[\frac{1}{|T(\omega)|}\cos[\Phi(\omega)] - 1\right]$$

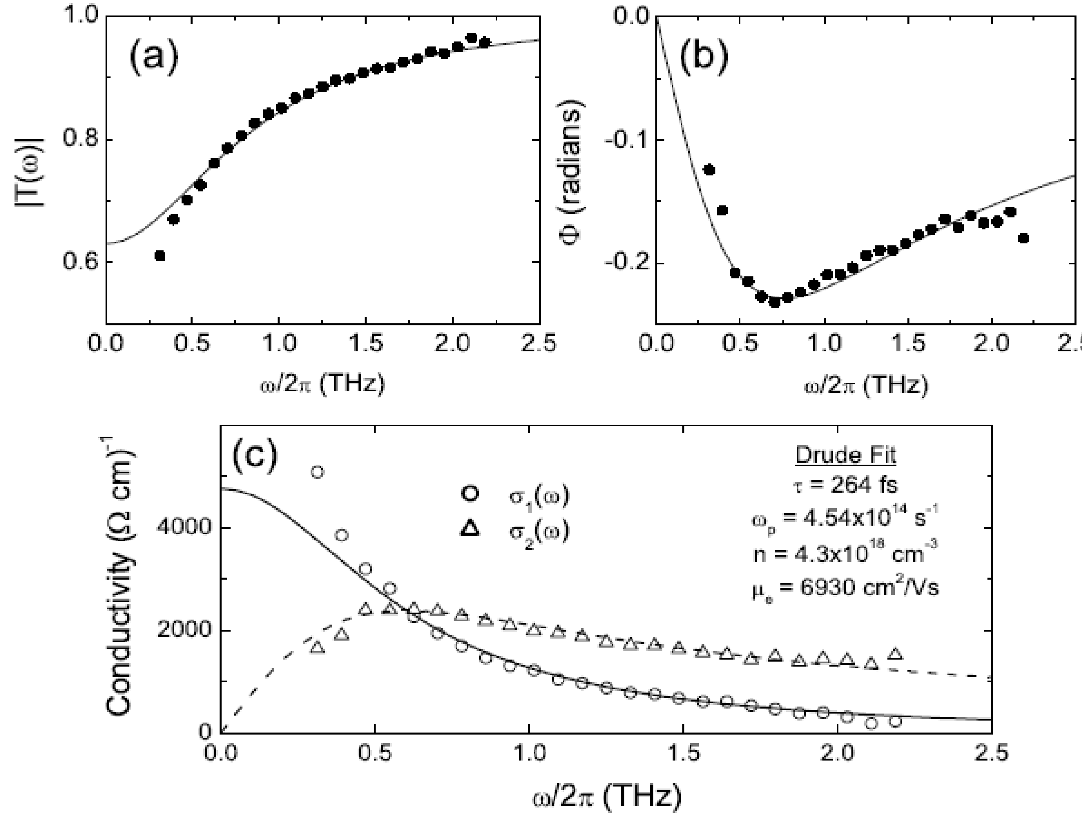
$$\Delta\sigma_s''(\omega) = -\frac{N+1}{Z_0}\left[\frac{1}{|T(\omega)|}\sin[\Phi(\omega)]\right]$$

Thin film approximation: Tinkham equations for photoexcited carriers

F. A. Hegmann, and K. P. H. Lui, Proc. SPIE **4643,** 31 (2002)

3D: Photoexcited GaAs

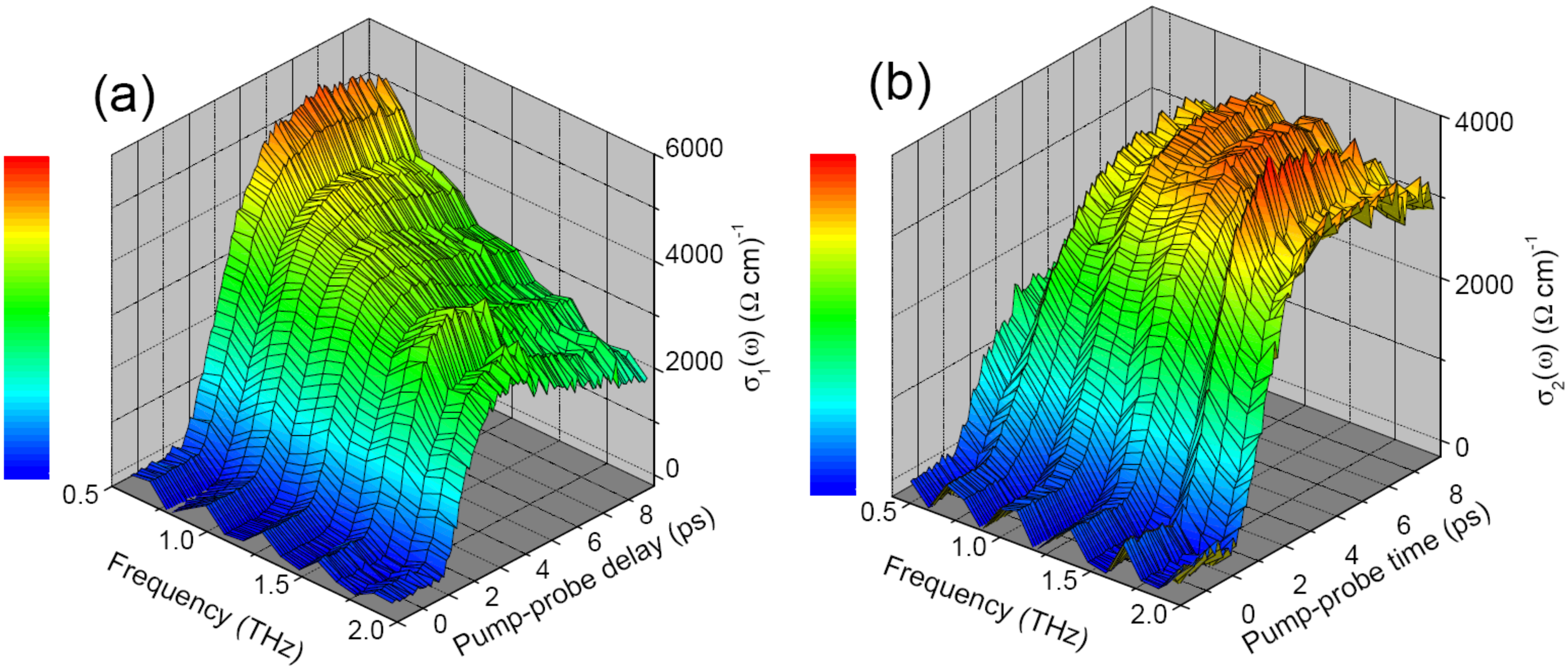




Carriers in GaAs are well described by Drude model just picoseconds after photoinjection.

$$\hat{\sigma}(\omega) = \frac{Ne^2\tau}{m}\frac{1}{1-i\omega\tau}$$

Time-dependent Drude parameters

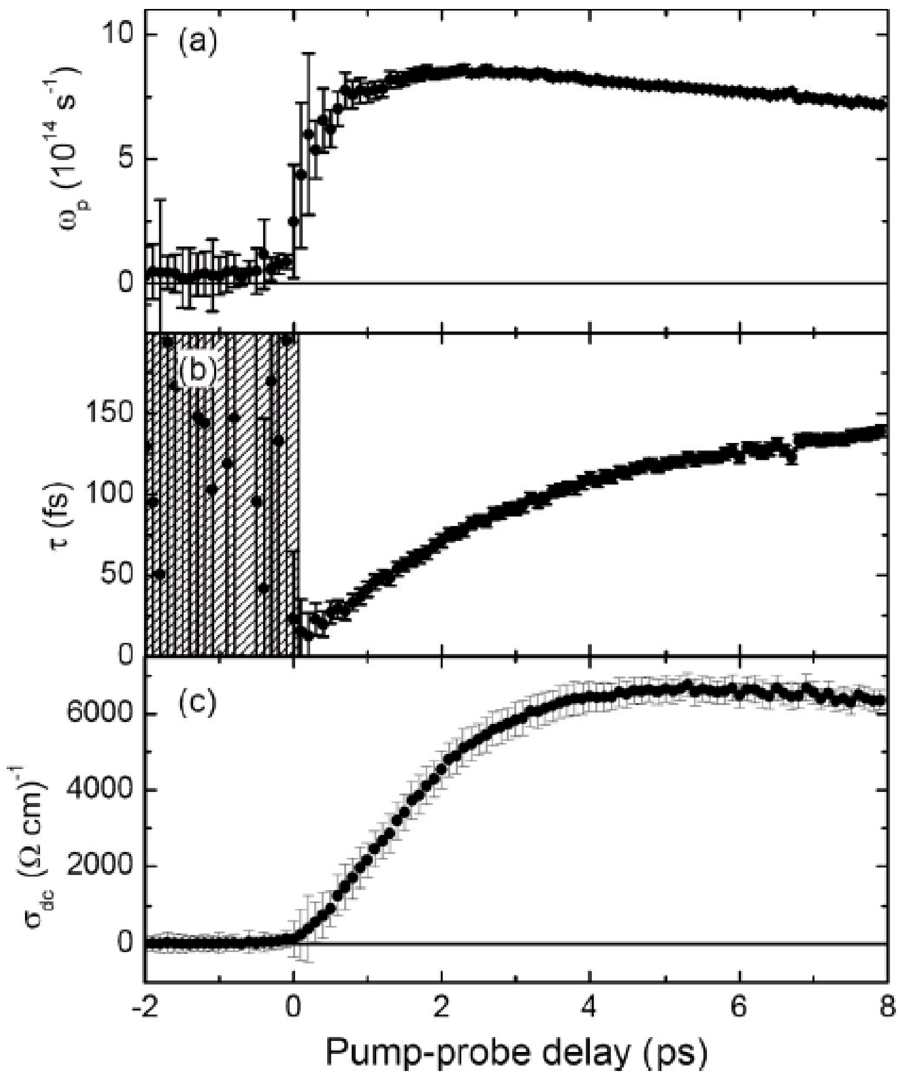


- Fit Drude model expression to data for increasing delay t_{pp}
- Time dependence of the Drude parameters
- Example: semi-insulating GaAs excited @ 400 nm

P. U. Jepsen, D. G. Cooke and M. Koch, Laser Photon. Rev. **5,** 124-166 (2011).

Time-dependent Drude parameters

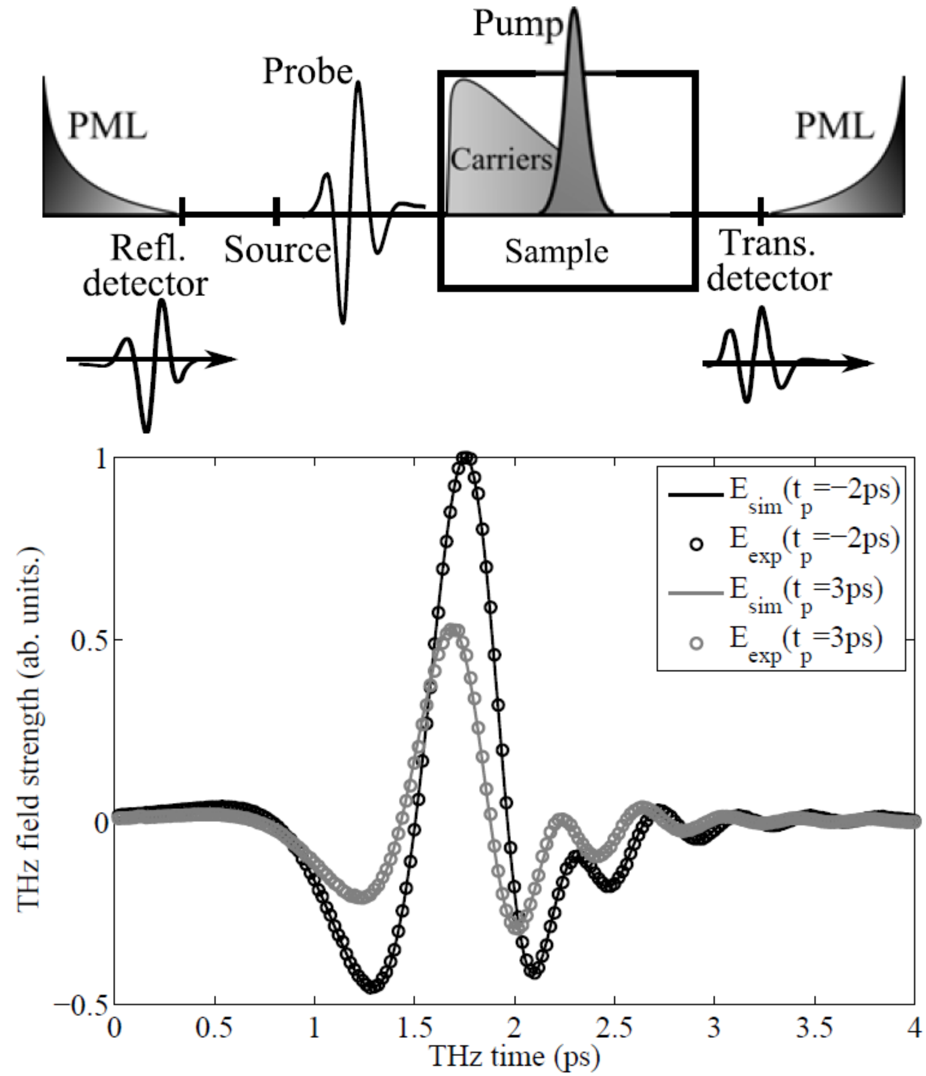
- Fit Drude model expression to data for increasing delay t_{pp}
- Time dependence of the Drude parameters
- Example: semi-insulating GaAs excited @ 400 nm
- Parameter extraction reveals the (here: known) carrier dynamics
- Instant rise of plasma frequency
- Slower rise of scattering time
- Slower rise of DC conductivity



P. U. Jepsen, D. G. Cooke and M. Koch, Laser Photon. Rev. **5,** 124-166 (2011).

FDTD simulation of TRTS

- In some situations the simple Fourier transform spectroscopy approach is not sufficient to understand the THz-TDS data
- Time-resolved spectroscopy near $t_{pp} = 0$
- Diffusion of charges in the sample during measurement
- Master student Casper Larsen coded a TRTS experiment in FDTD
- Thorough comparison between FDTD and experiment
- GaAs, 800 and 400 nm excitation
- Carrier dynamics explicitly included in code
- Full description of dispersion, diffraction, phase mismatch



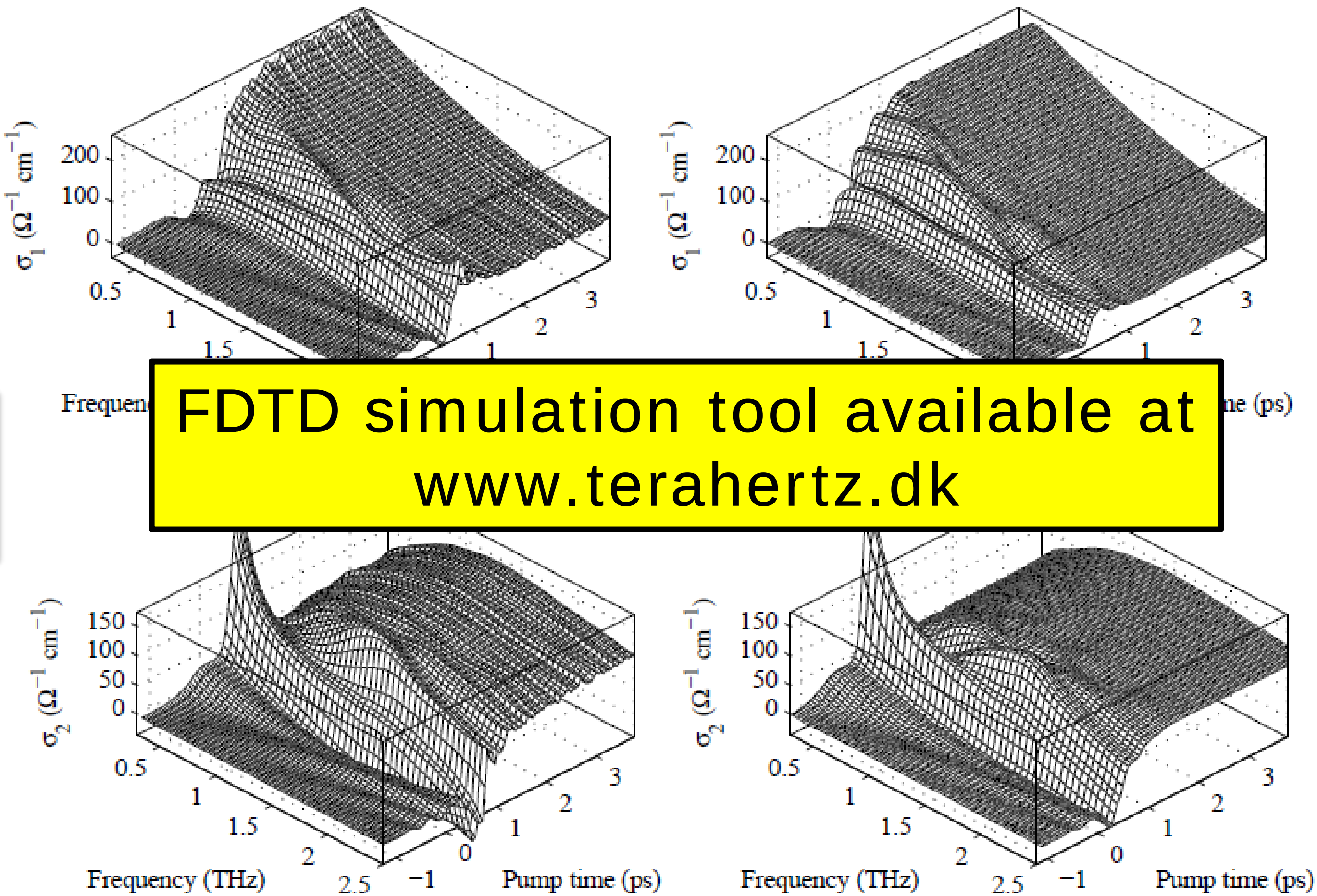
C. Larsen, D. G. Cooke and P. Uhd Jepsen
J. Opt. Soc. Am. B **28,** 1308 (2011)

Simulation vs experiment

$\sigma_1(\omega, t_{pp})$

$\sigma_2(\omega, t_{pp})$

7 µJ/cm²
800 nm
45 fs



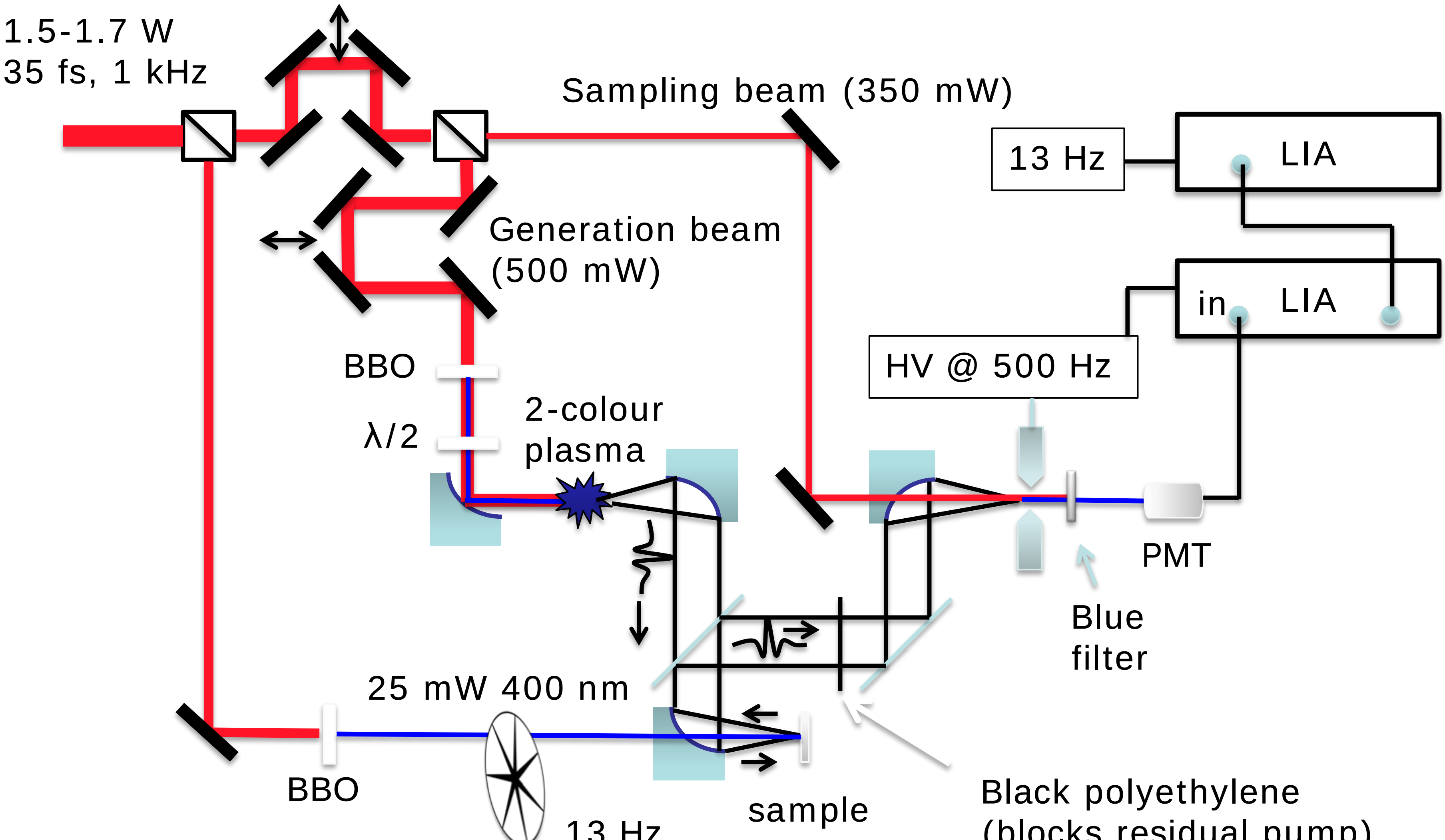
FDTD simulation tool available at www.terahertz.dk

(a) Experiment

(b) Detector and aperture

C. Larsen, D. G. Cooke and P. Uhd Jepsen
J. Opt. Soc. Am. B **28,** 1308 (2011)

Air Plasma Time-resolved THz Spectrometer



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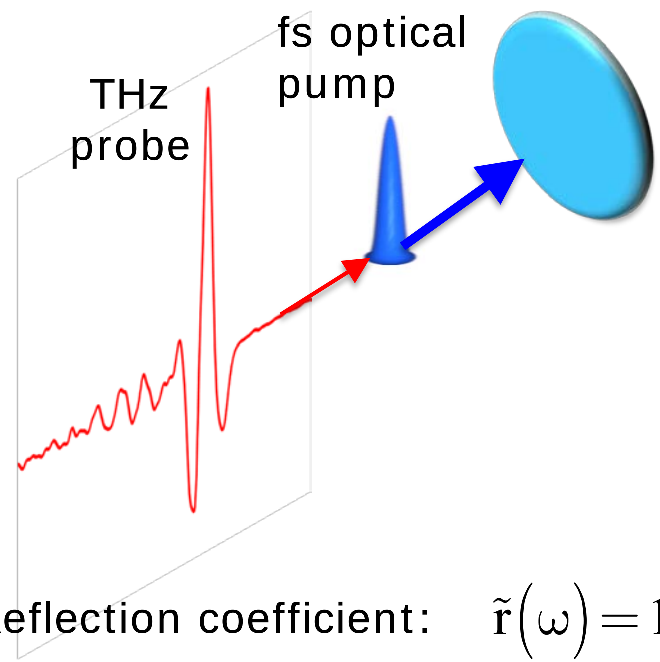
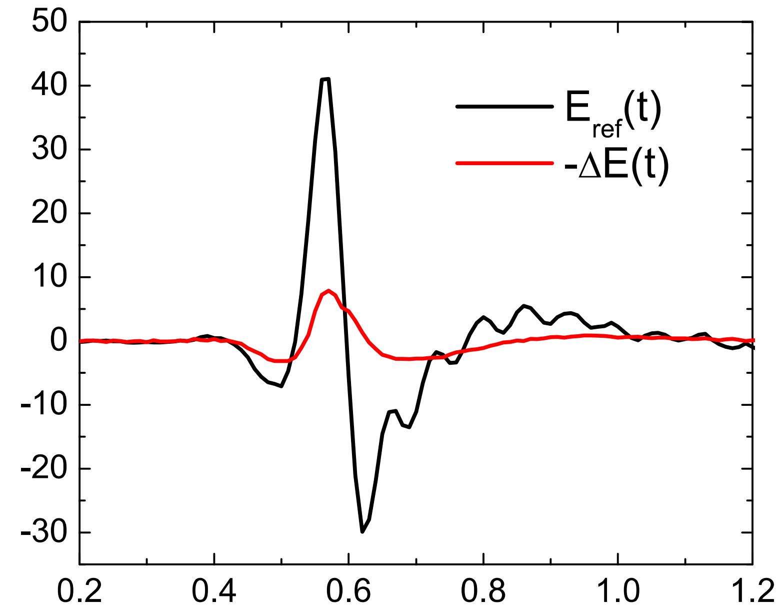
ABCD:
J. Dai, X. Xie, X.-C. Zhang PRL **97,**103903 (2006)

Experiment in reflection

- 400 nm pump – THz probe
- F_{400nm} = 800 μJ/cm²



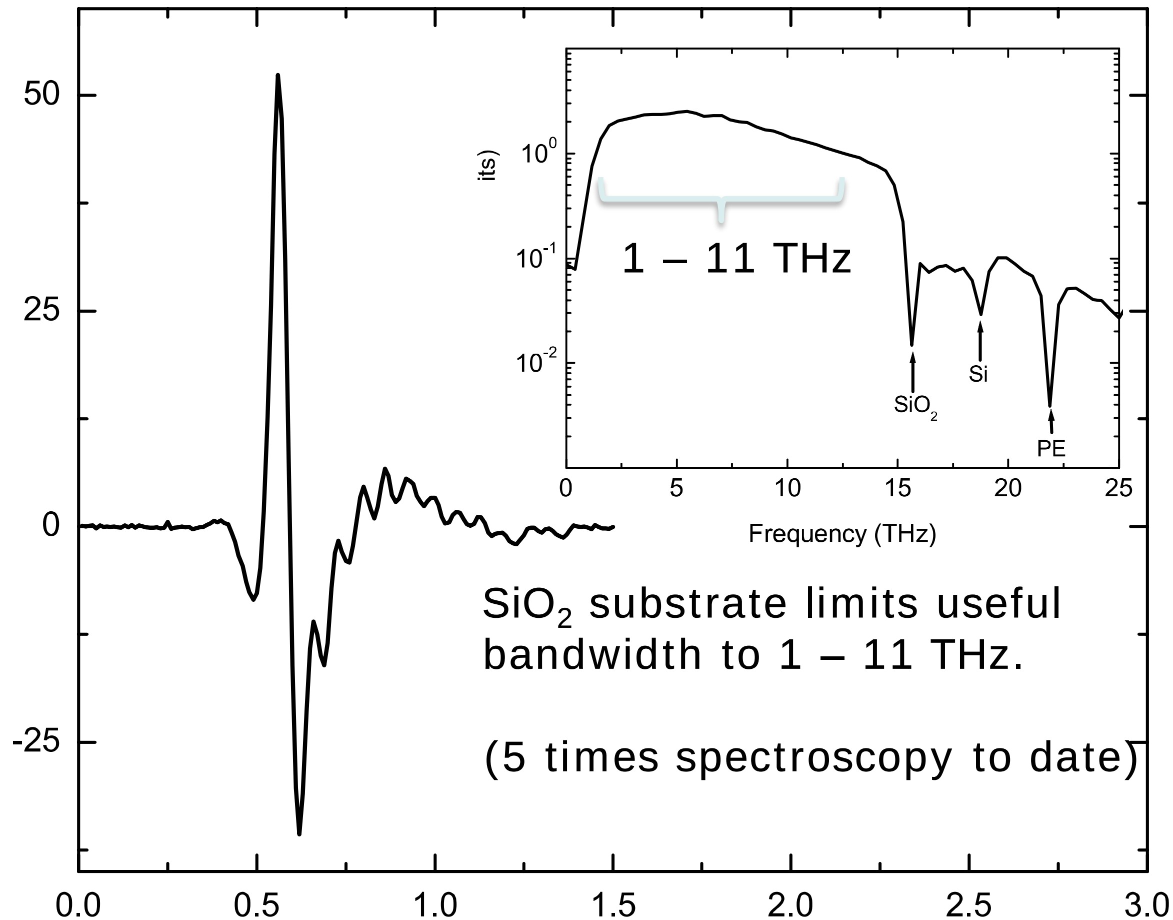
Simultaneous acquisition of $E_{ref}(t)$ and $-\Delta E(t)$



Reflection coefficient:
$$\tilde{r}(\omega) = 1 + \frac{\Delta E(\omega)}{E_{ref}(\omega)} = \frac{1 - n(\omega) - Z_0 d\tilde{\sigma}(\omega)}{1 + n(\omega) + Z_0 d\tilde{\sigma}(\omega)} \left[\frac{1 + n(\omega)}{1 - n(\omega)} \right]$$

$n(\omega)$ is SiO_2 substrate index

Spectrometer performance



SiO_2 substrate limits useful bandwidth to 1 – 11 THz.

(5 times spectroscopy to date)

Drude and non-Drude conductivity

- Drude model:
  Mean free path $l = v_F \tau$ (Fermi velocity)
- What could happen if carriers are confined to $d < l$
- Enhanced backscattering
- Can be phenomenologically modelled by the Smith generalization

$$\tilde{\sigma}(\omega) = \frac{Ne^2\tau/m_{eff}}{1 - i\omega\tau}\left[1 + \sum_{n=1}^{\infty} \frac{c_n}{(1 - i\omega\tau)^n}\right]$$

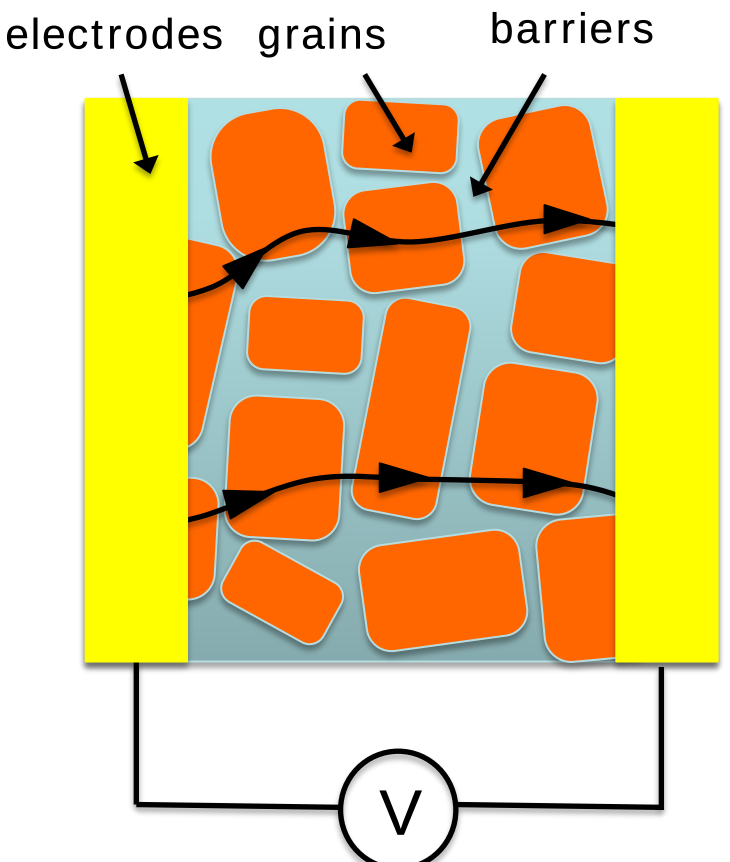
- Generalized current response function *j(t)*. Truncate to first order
- Kramers-Kronig compatible (causal response function)
- Parameter *c:* degree of backscattering
- Parameter *c:* reflection coeffient at boundary
- Parameter *c:* first-order Taylor coefficient of generalized impulse response

$$j(t) = f(t)e^{-t/\tau}\ , \quad c_n = \partial^n f/\partial t^n|_{t=0}$$

N. V. Smith, Phys. Rev. B. **64,** 155106 (2001)
H. Nemec et al, Phys. Rev. B **79,** 115309 (2009)

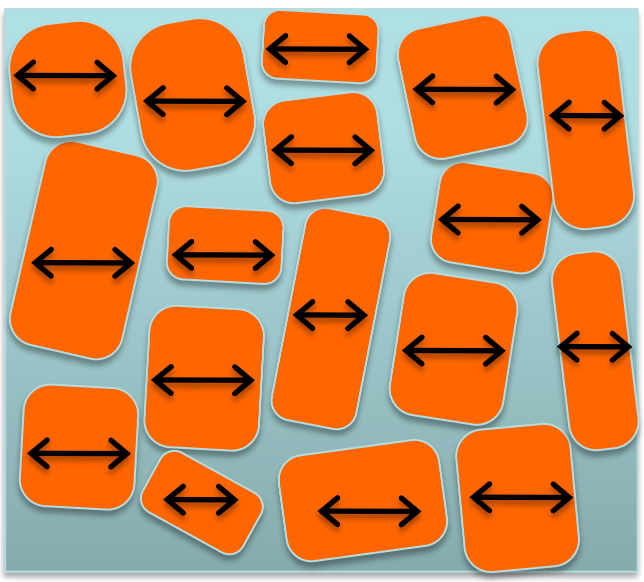
Conductivity in disordered media

dc measurement



dc conductivity is determined by the highest barrier in conduction path

ac measurement



$$L_\omega = \sqrt{\frac{D}{\omega}}$$

Smaller conducting grains can contribute more to conductivity at higher ω.

Silicon nanocrystals in glass

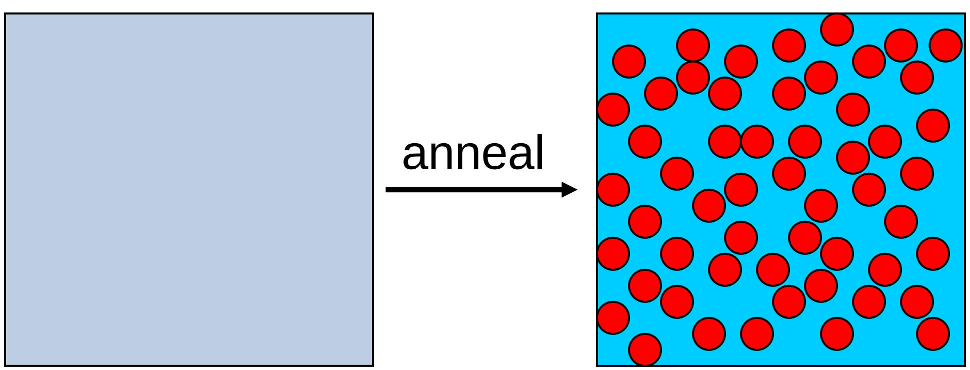
200 nm / 1 micron SiO_x on SiO_2 substrates

Annealed at 1100 C, 1 atm 95% N_2 + 5% H_2

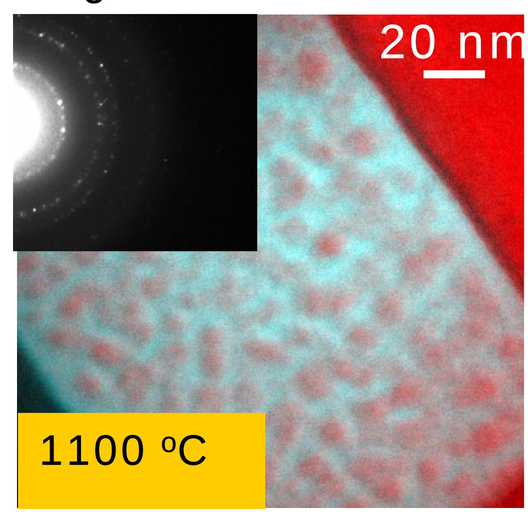
⇒Thermal decomposition of non-stoichiometric oxide: Si nanocrystals in SiO_2

$$SiO_x \Rightarrow SiO_2 + Si$$

Variable NP density: $VF_{Si} = \dfrac{(2-x)V_{mol}^{Si}}{xV_{mol}^{SiO_2} + (2-x)V_{mol}^{Si}}$



High-resolution TEM



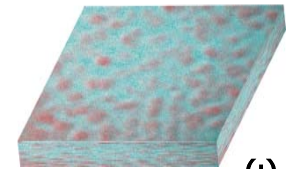
x = 1.0 (31% silicon)

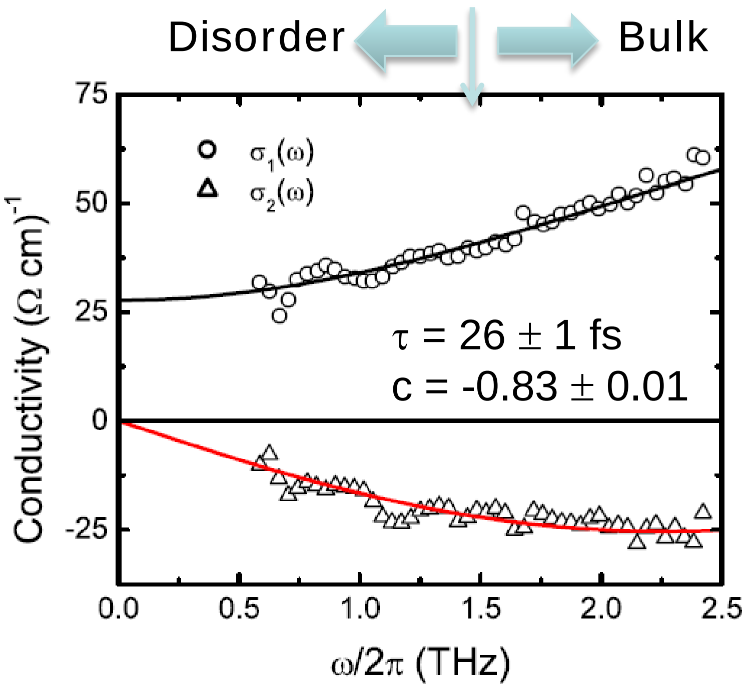
Low bandwidth measurements

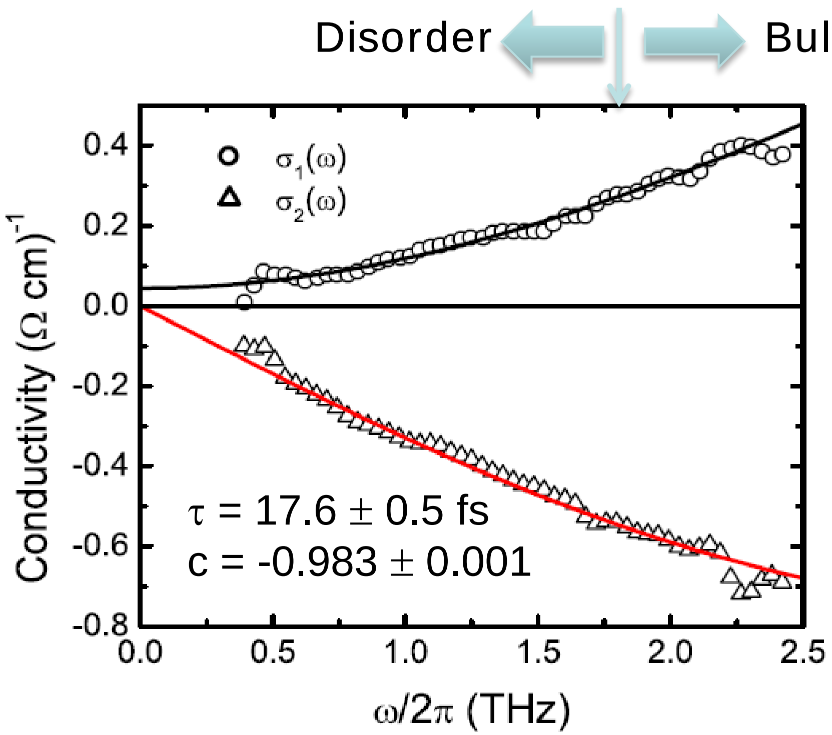
poly-nc Si

inter-connected Si grains (~20 nm)

Si-NCs in glass



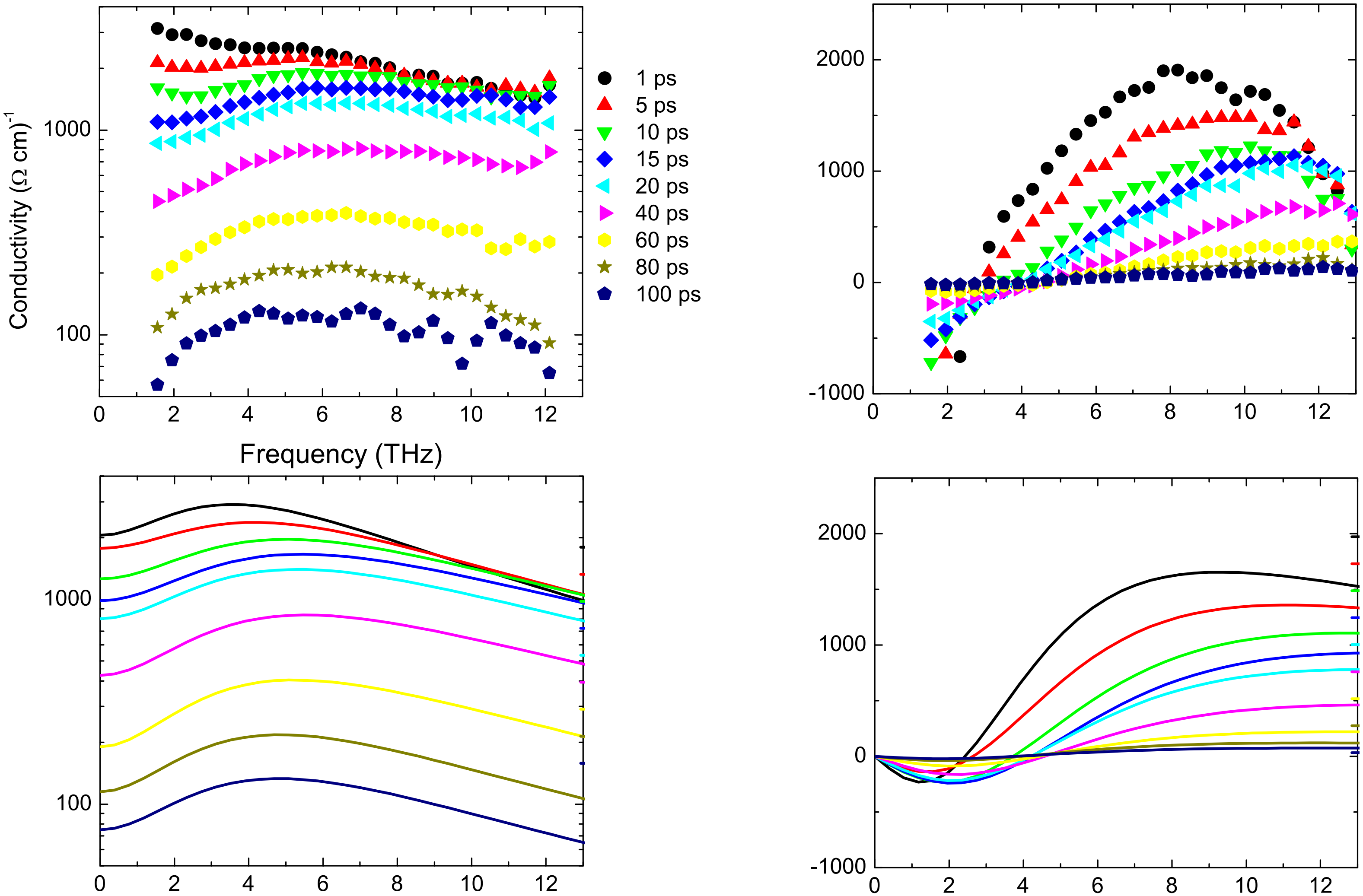




Fused silica substrate cuts off transmission above 3 THz. **Reflection measurements**

D. Cooke et al., Phys. Rev. B **73**, 193311 (2006).
L. Titova et al., Phys. Rev. B **83**, 085403 (2011).

Conductivity dynamics: $SiO_{x=0.2}$

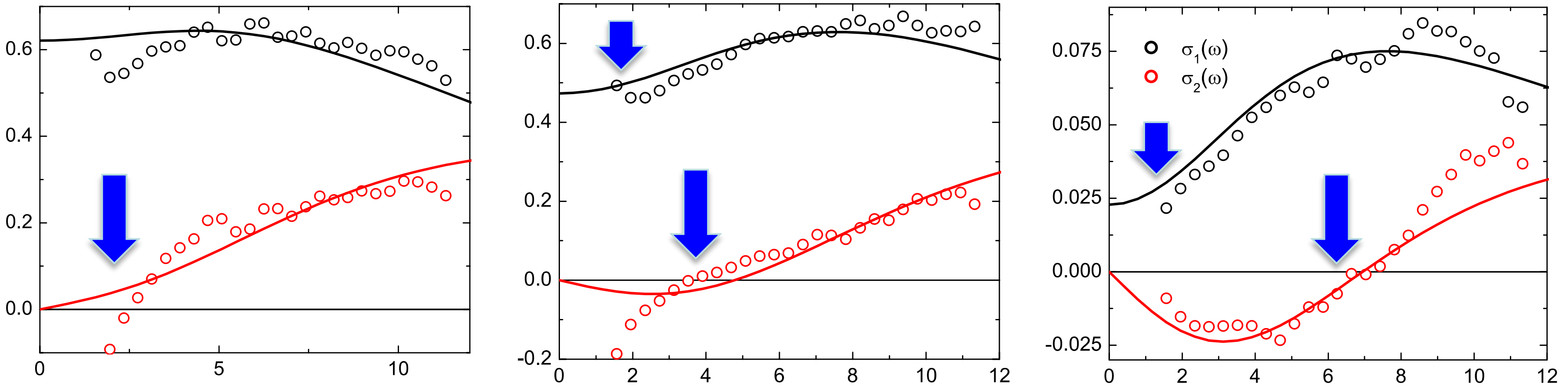


Drude behavior at early times

Evolution of conductivity: from Drude to partially localized response

$SiO_{x=0.6}$ (51% silicon)

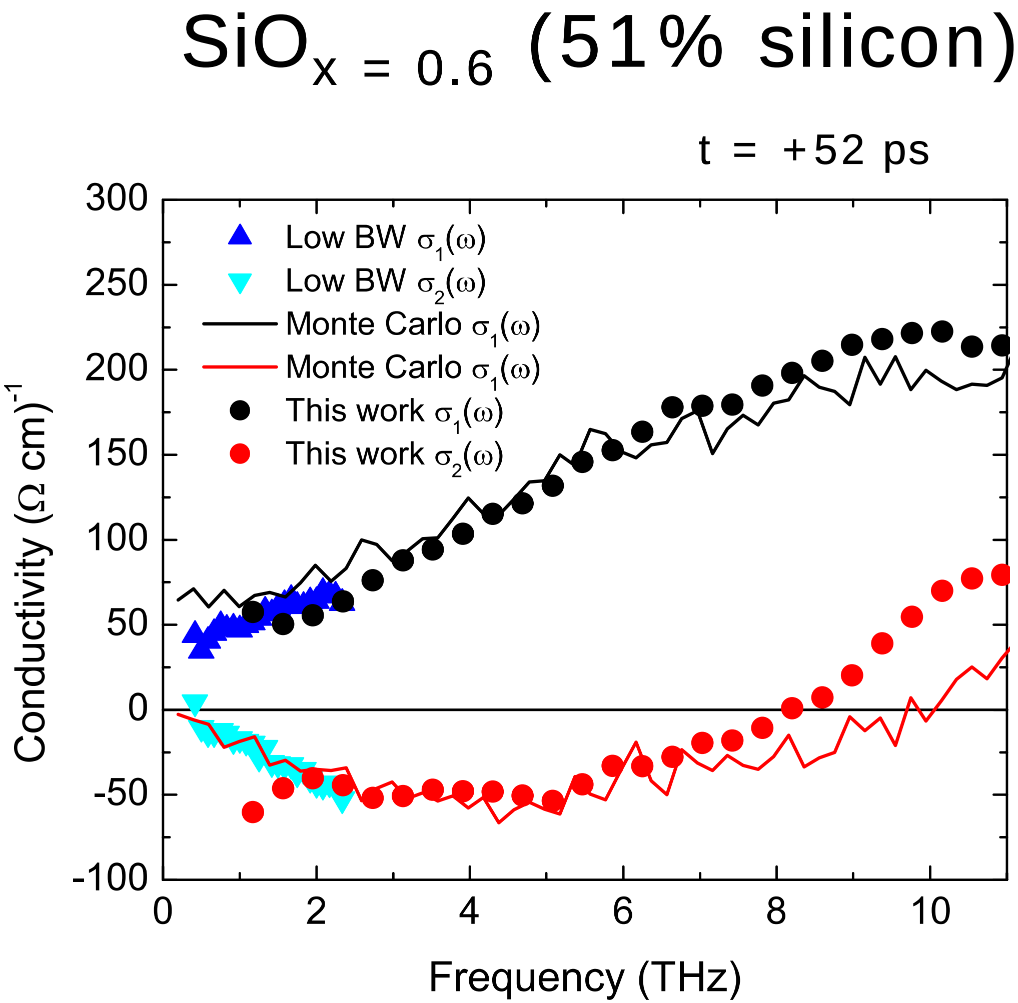
t = 0.5 ps   t = 2.0 ps   t = 100 ps



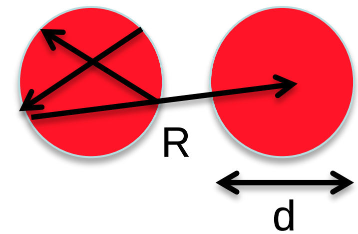
Drude-like behavior at early times!
Carriers have yet to "feel" their confinement.

Partially localized
Long range conduction limited by SiO_2 barriers

Agreement with previous work



Random sampling and no scaling of data



Monte Carlo parameters:

Reflection at particle boundary: R = 85%

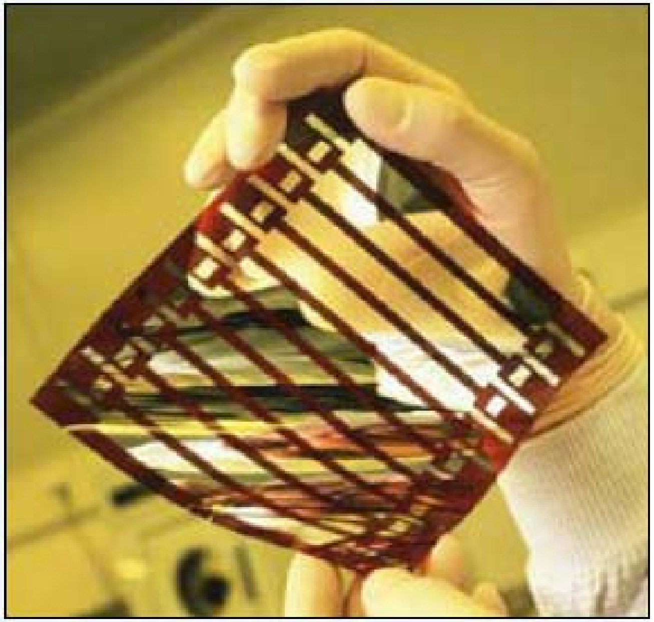
Particle diameter = 10 nm

(courtesy of F. Hegmann group, Univ. Alberta, CA)

Excellent agreement with both low bandwidth work and Monte Carlo simulations

Plastic Photovoltaics

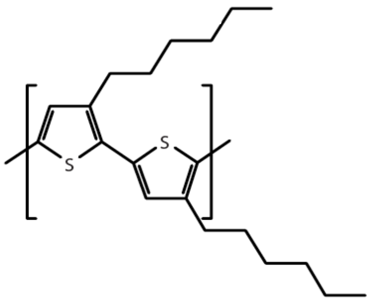
- Solution processed
- Lightweight
- Cheap to manufacture
- Compatible with large scale processing
- Fundamental excitation thought to be an exciton.
- Exciton $E_B > k_BT$
- Device performance depends on charge generation through exciton dissociation.
- **Ultrafast charge generation mechanism is a topic of huge debate, fueled by transient absorption and fs flourescence upconversion.**
- **THz spectroscopy can contribute significantly here**



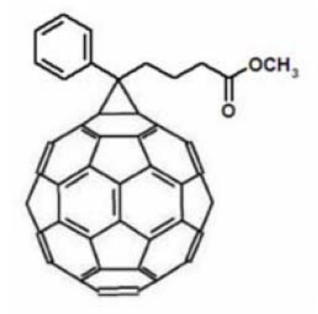
Organic materials promise inexpensive flexible solar fabric for powering personal electronics or for integration into buildings. Source: BRN Solar Report, Konarka

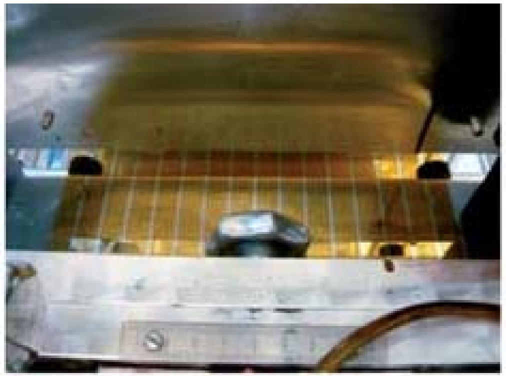
P3HT/PCBM roll-to-roll processed films

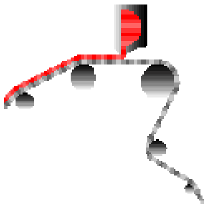
Poly-3-HexylThiophene



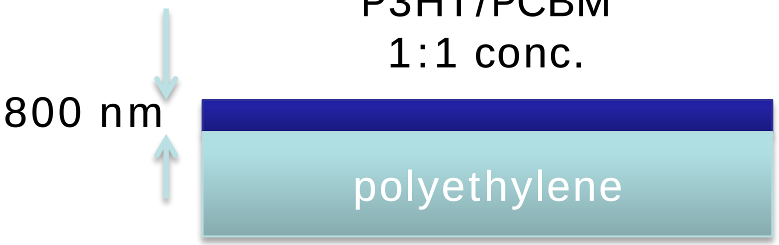
[6,6]-Phenyl-C61 Butyric acid Methyl ester







P3HT/PCBM
1:1 conc.



400 nm photoexcitation
Fluence = 570 μJ/cm^2

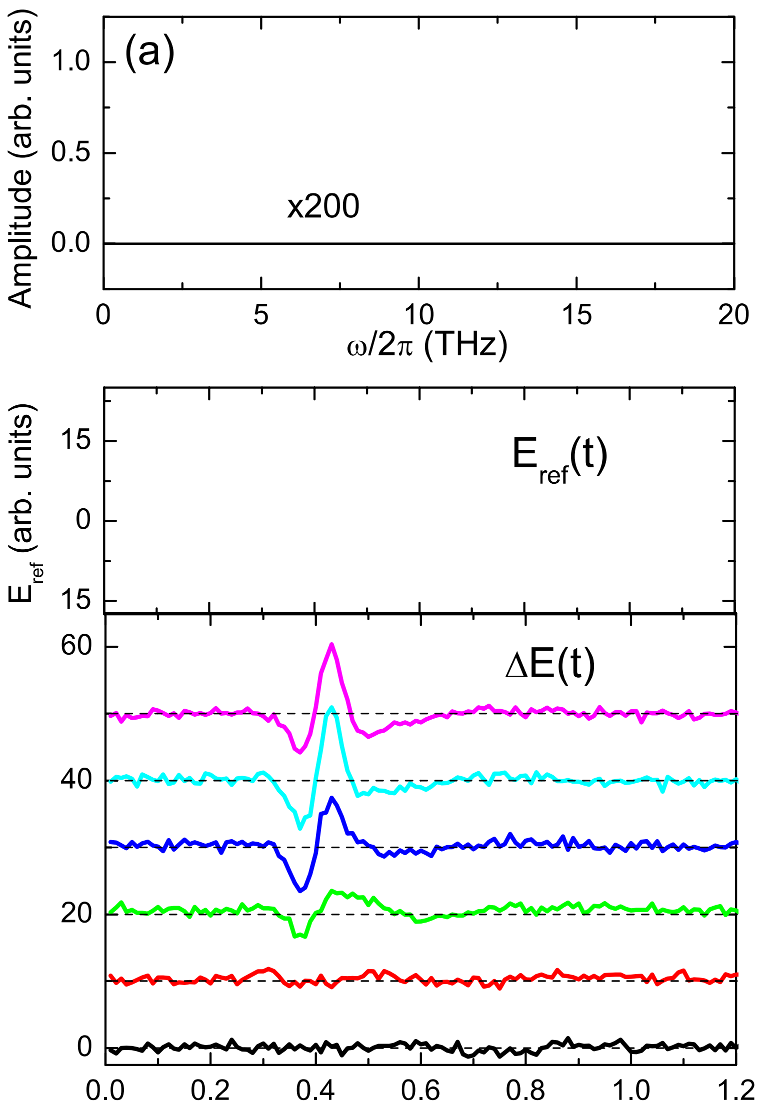
Measure on a real device-ready film!

Differential THz scans at early times

Reference and differential spectra:

Reference pulse:

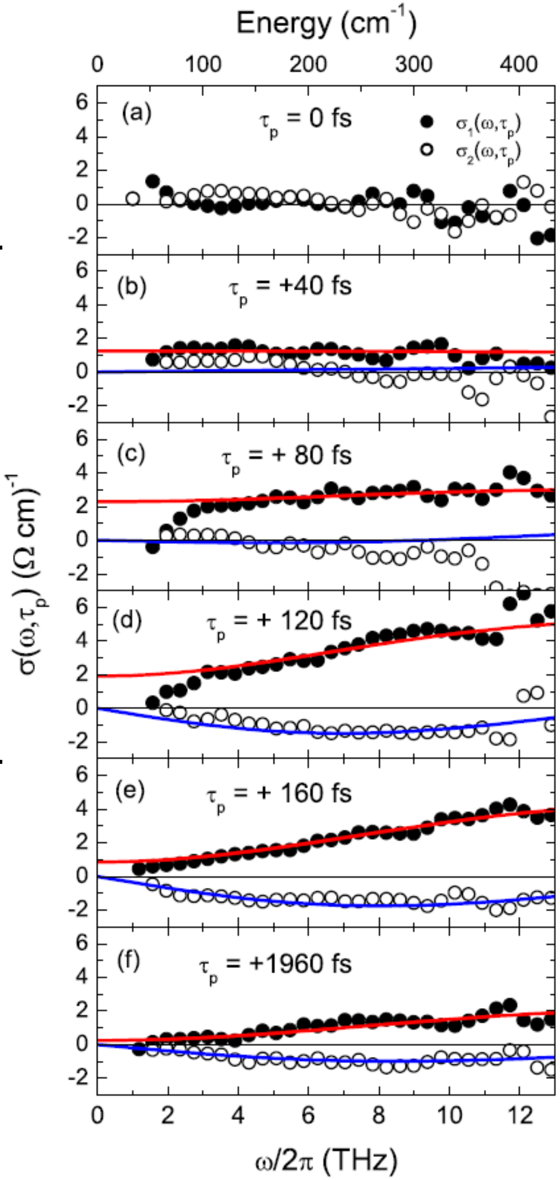
Differential pulses:

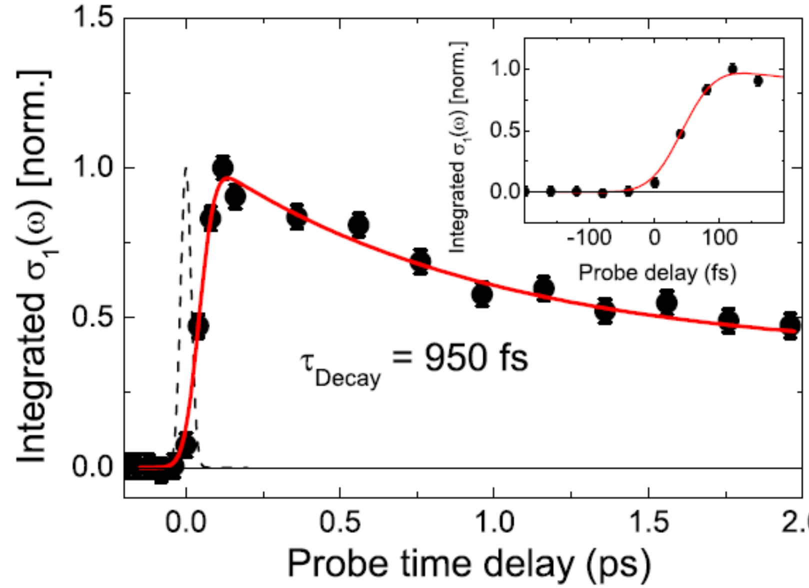


Sub-100 fs THz conductivity

Non-zero real conductivity is signature of mobile charges (delocalized polarons)

Free charges first 120 fs





Mobile charges created within 75 fs of excitation.
("Hot" exciton dissociation likely)

Then: re-trapping of charges (~120 fs)

Later: 1/3 free charges
2/3 trapped charges

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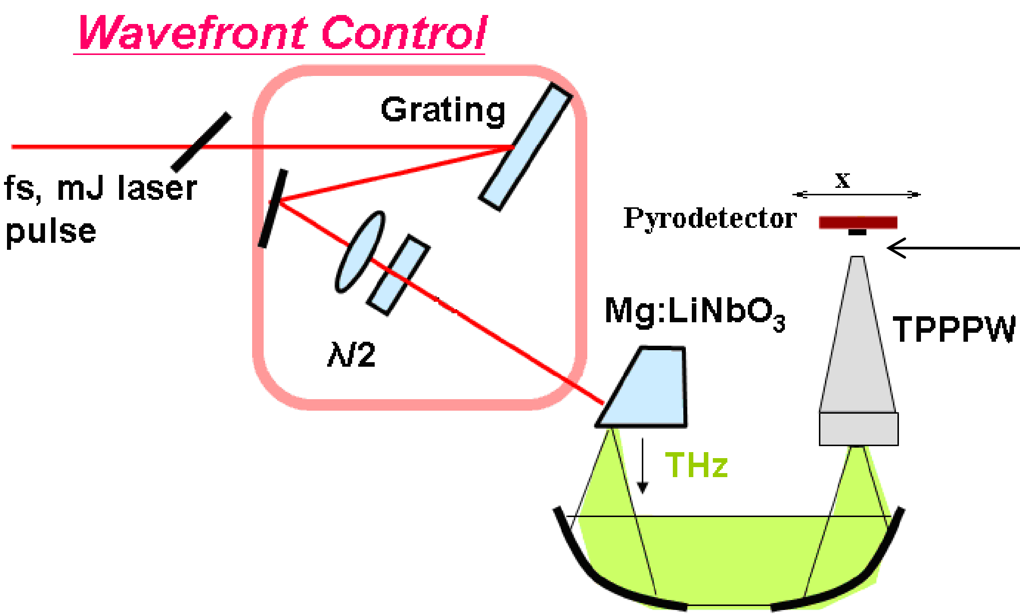
D. G. Cooke, F. Krebs, P. U. Jepsen, submitted (2011)

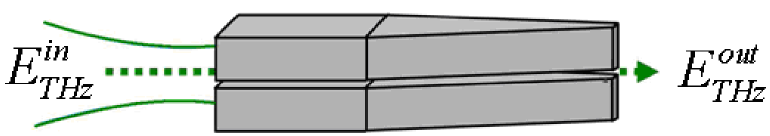
Field enhancement in waveguides

Challenge: Get high enough THz field strength for NLO at THz frequencies

Here: Adiabatic compression of the field in a PPWG

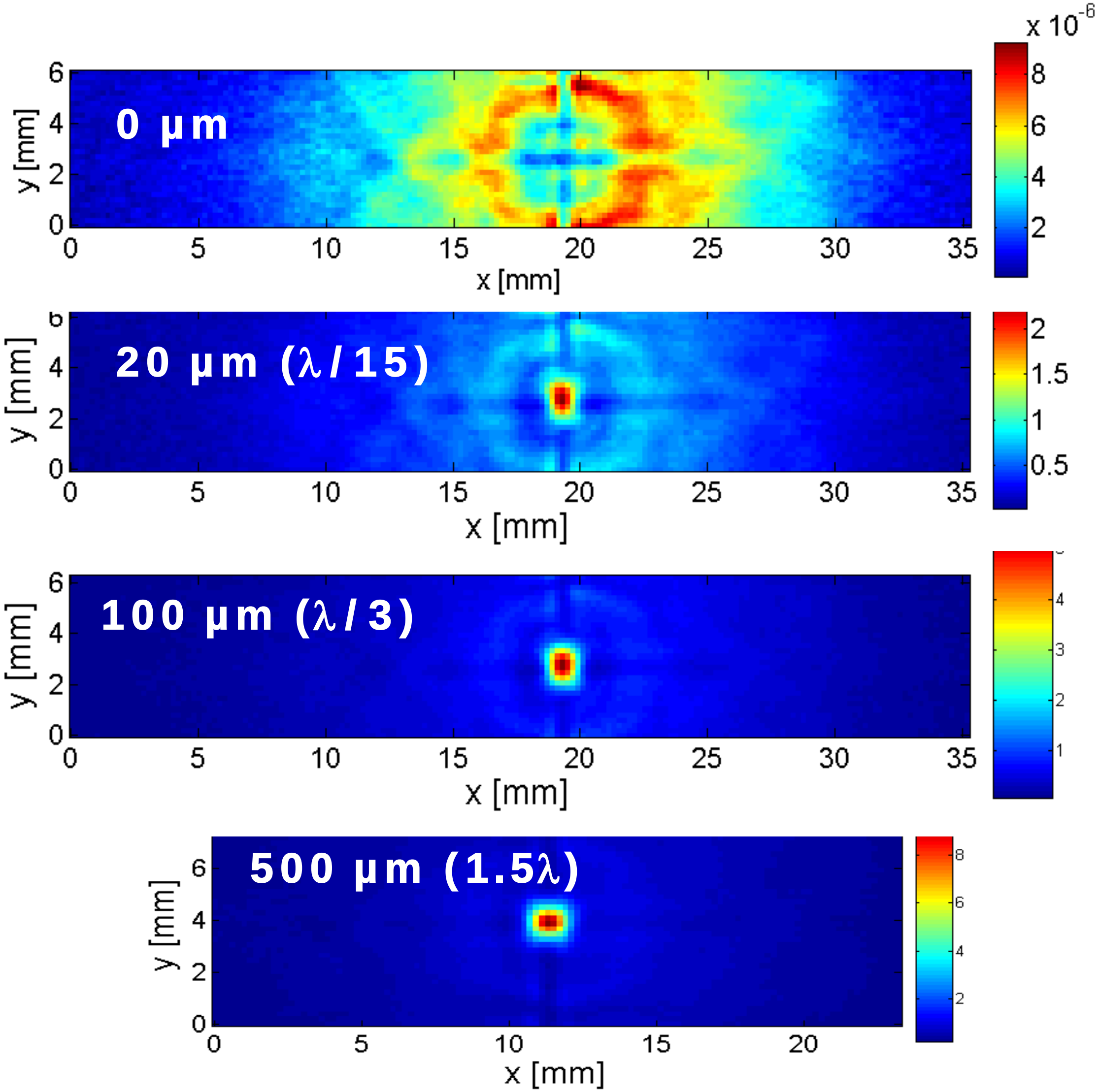


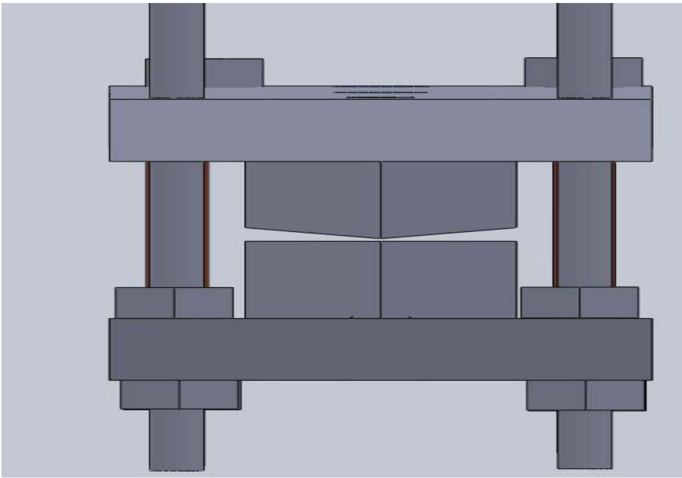
Perform NLO experiments at the WG tip!



Iwaszczuk, Zhang, Jepsen, in preparation

Field compression





In contact:
no light through the tip

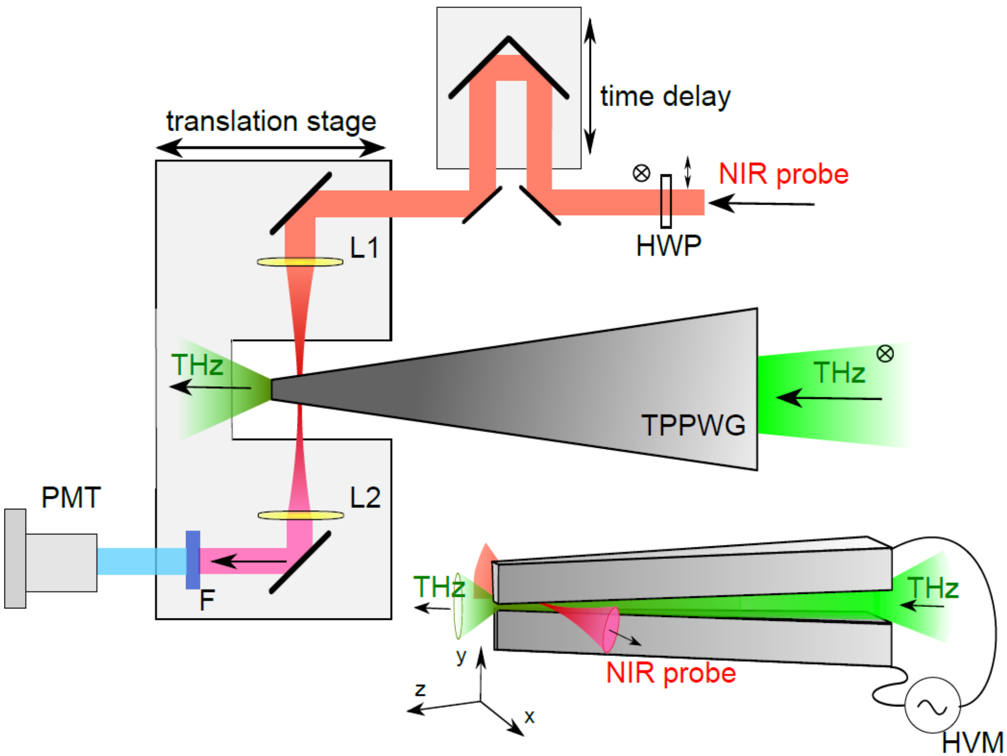
Sub-λ gaps:
significant field at the tip

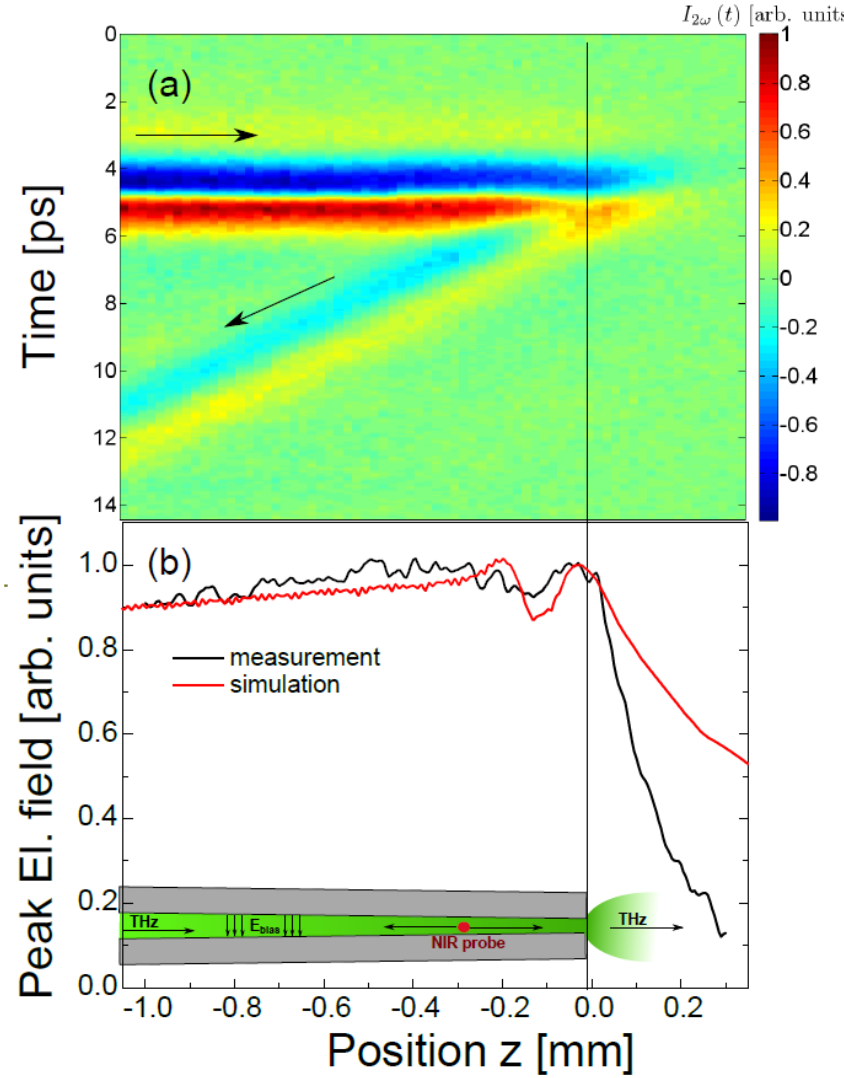
>λ gaps:
very high transmission

K. Iwaszczuk *et al*, in preparation

Measurement of the THz field strength

- THz-enhanced SHG ($\chi^{(3)}$ process)
- Calibrated measurement of field strength





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K. Iwaszczuk *et al*, Appl. Phys. Lett. **99, 071113 (2011).**

Calibration of E-field measurement

SHG in the presence of a THz field and a static field:

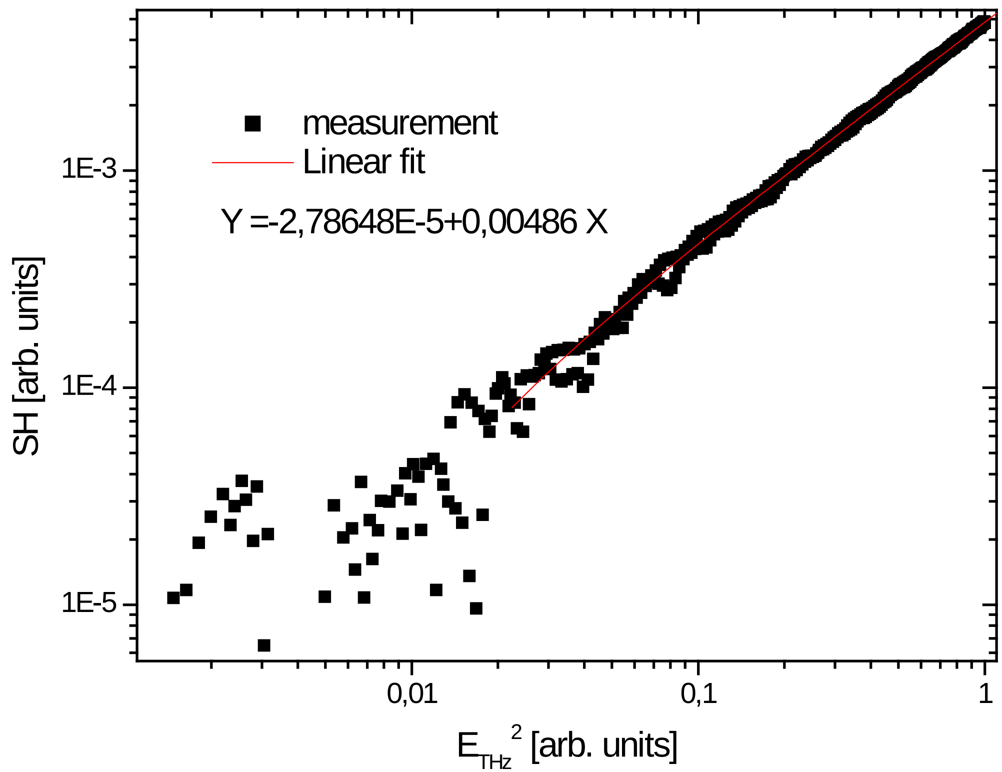
$$I_{2\omega} \propto \left(\chi^{(3)} I_{\omega}\right)^{2} \left[\left(E_{THz}\right)^{(2)} + 2E_{bias}E_{THz} + \left(E_{bias}\right)^{2}\right]$$

Modulate the THz field, use lock-in detection:

$$I_{2\omega} \propto \left(E_{THz}\right)^{2} + 2E_{bias}E_{THz}$$

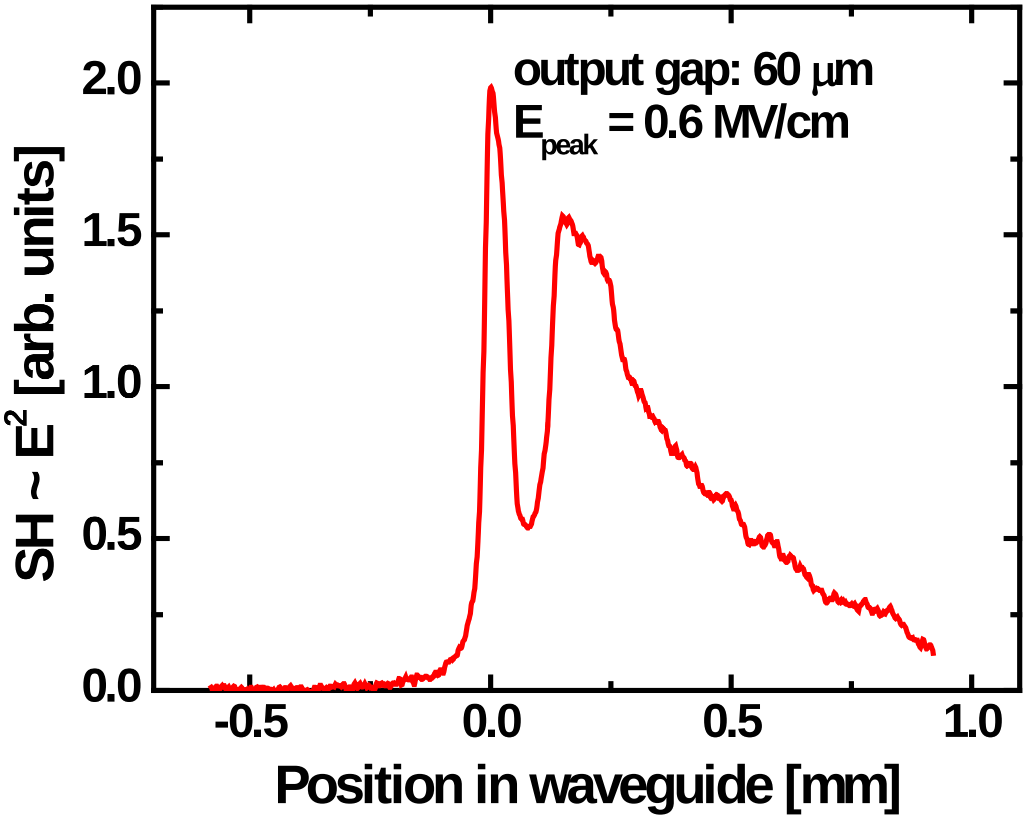
Modulate bias voltage, change of SH gives THz field strength:

$$dI_{2\omega} / dE_{bias} = 2E_{THz}$$



K. Iwaszczuk *et al*, in preparation

Results: E_{THz} = 1.4 MV/cm at WG tip



- Good agreement with full vectorial simulations
- >1.4 MV/cm obtained with 20 μm gap
- 100 kV/cm input field strength

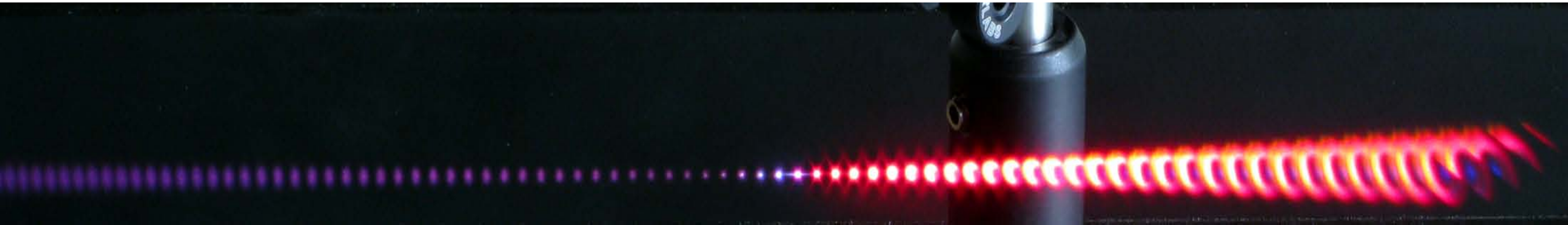
K. Iwaszczuk *et al*, in preparation (2011)

Conclusions

- THz spectroscopy is a good way to measure photoconductivity
- Complex conductivity spectrum is measured
- Conductivity models can be tested
- Disordered systems show clear non-Drude behaviour
- Ultrafast time resolution is important to reveal detailed dynamics

Acknowledgements:
Krzysztof Iwaszczuk (PhD student, DTU Fotonik)
Casper Larsen (Master student, DTU Fotonik)
Prof. X.-C. Zhang (Rensselaer Polytechnic Institute)

Funding:
Carlsberg Foundation
Danish Defence Acquisition and Logistics Organization
H. C. Ørsted Foundation



New THz journal

New THz journal from IEEE!

Each issue features interview articles with THz pioneers – March issue will host an interview with Nobel Laureate Bob Wilson.

Get a technical paper in the same issue!

Submissions at
http://mc.manuscriptcentral.com/ieee-thz

Upcoming conferences

Submission Deadline: December 5th

http://www.cleoconference.org/

CLEO:2012

Technical Conference: 6-11 May 2012 Exposition: 8-10 May 2012

San Jose Convention Center, San Jose, CA, USA

CLEO: QELS—FUNDAMENTAL SCIENCE

CLEO: SCIENCE & INNOVATIONS

CLEO: APPLICATIONS & TECHNOLOGY

EOS European Optical Society

Coherence for Europe ®

Submission opens: January 16th 2012

Submission deadline: February 17th 2012

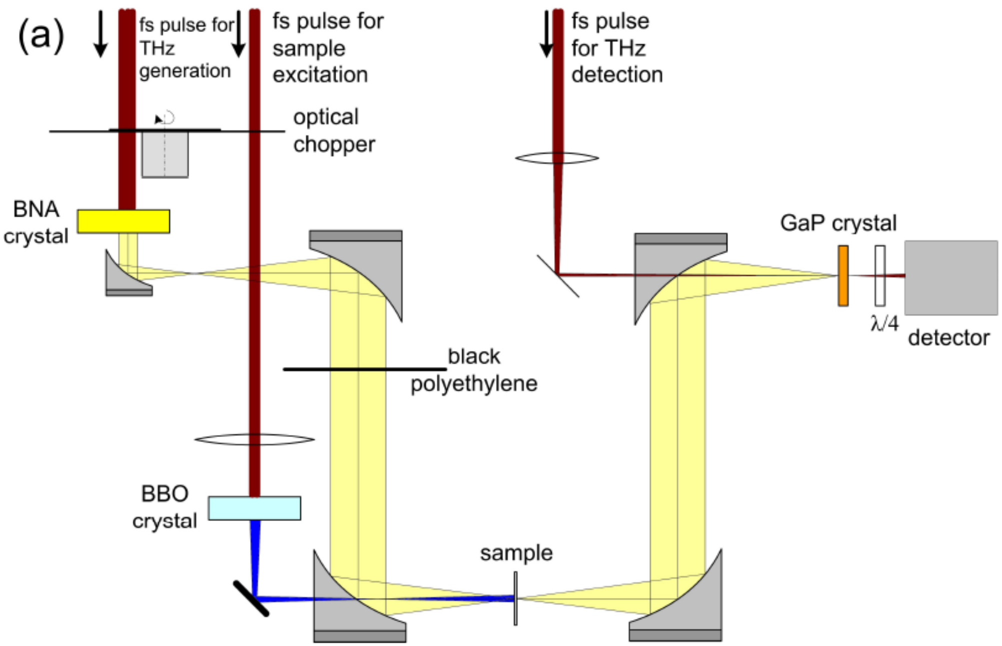
3rd EOS Topical Meeting

on THz Science & Technology (TST 2012)

17 - 20 June 2012

Kaiserstejnsky Palace, Prague, Czech Republic

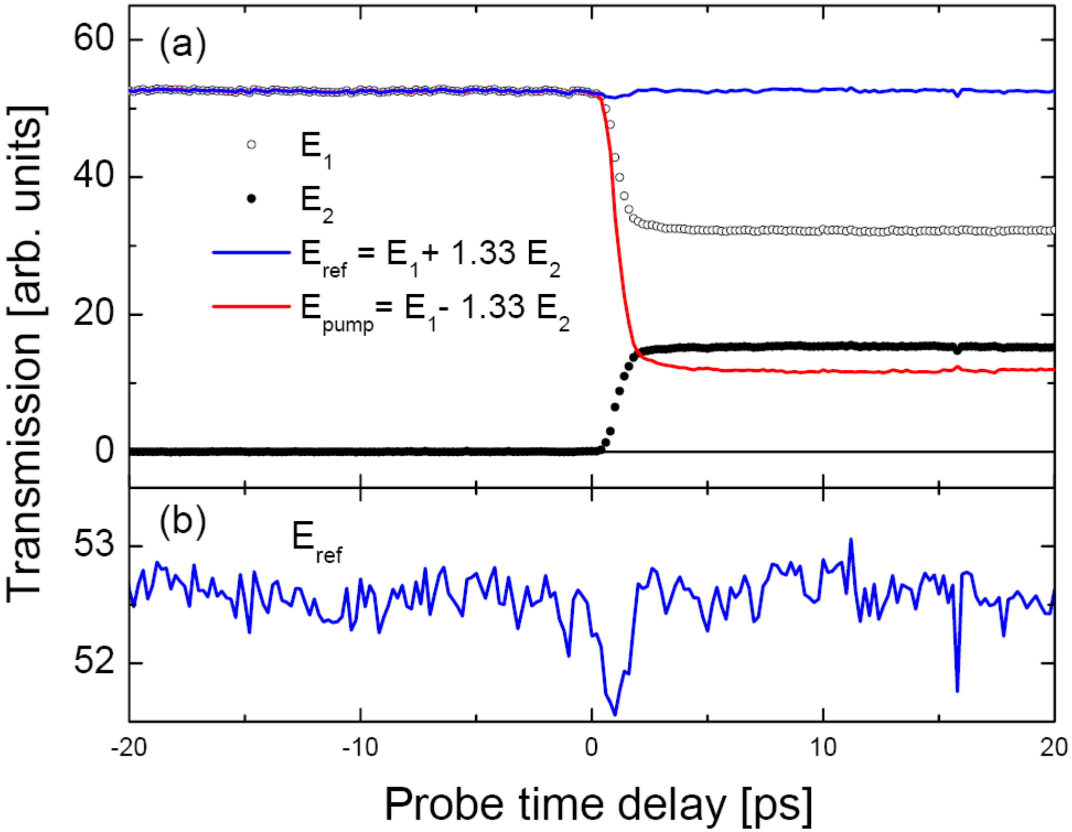
http://www.myeos.org/events/tst2012



- ”Normal” THz time-domain spectroscopy
  - record reference data set (”sample OUT”, or ”optical pump OFF”)
  - **then** record sample data set (”sample IN”, or ”optical pump ON”)
- Alternative scheme for time-resolved pump-probe measurements:
  - Record reference and sample data **simultaneously**
  - minimizes influence of drift, power fluctuation, pointing stability issues, etc.

K. Iwaszczuk *et al.*, Opt. Express **17,** 21969 (2009)

Dual lock-in scheme for data acquisition



$E_1(t)$ chopped at 333 Hz (2x167 Hz)

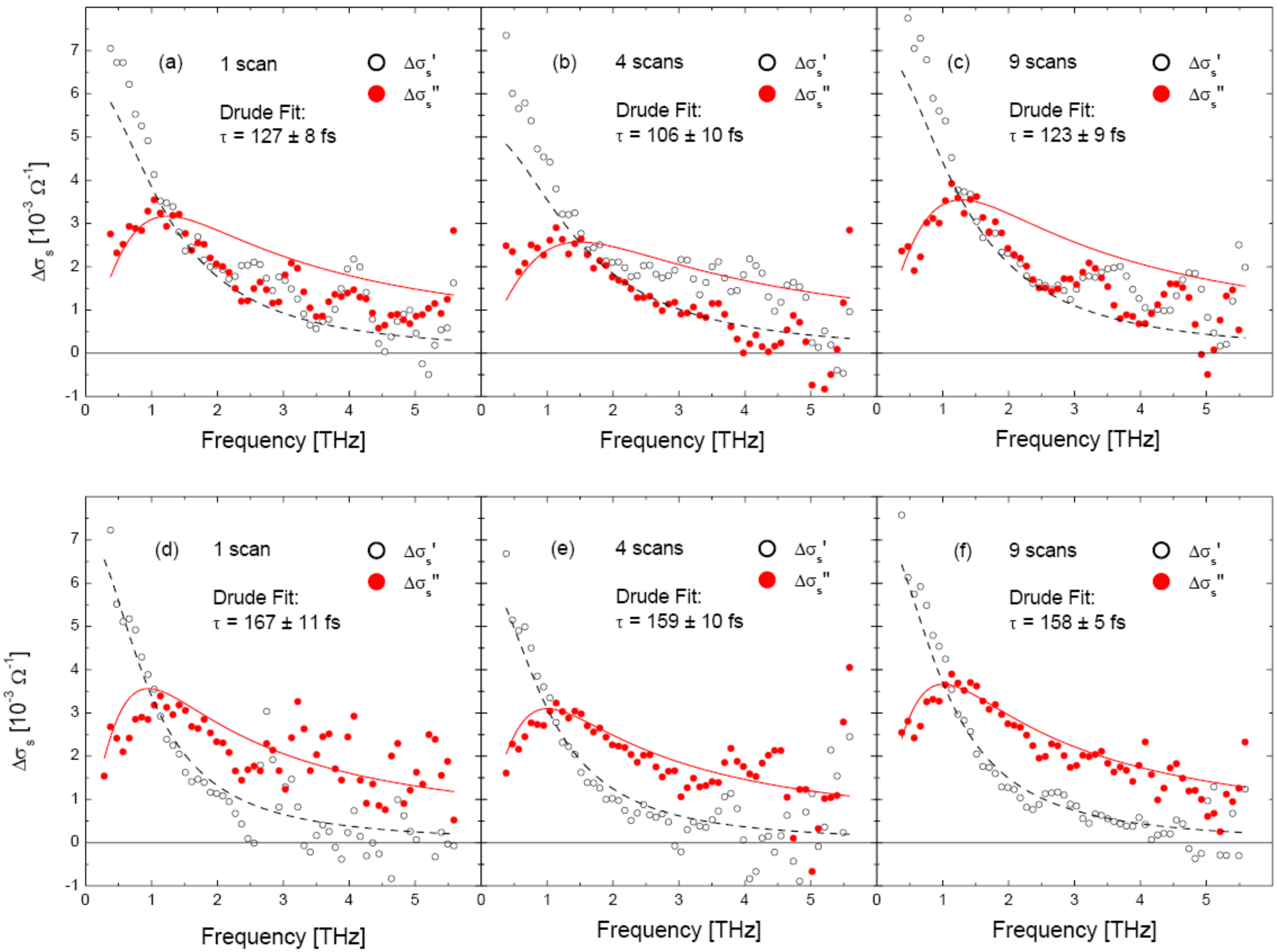
$E_2(t)$ chopped at 500 Hz (3x167 Hz)

$$E_{ref}(t) = E_1(t) + AE_2(t)$$
$$E_{pump}(t) = E_1(t) - AE_2(t)$$

A is a constant which depends on the experiment

(specifically the Fourier components at 2f and 3f of the PD signal in the EO sampling system)

K. Iwaszczuk *et al.*, Opt. Express **17,** 21969 (2009)



Sequential:

- Drude model cannot reproduce the spectra
- caused by minute (10-20 fs) jitter
- Experiment was placed in a room with poor temperature stability

Simultaneous:

- Drude model describes the spectra well
- no effect of jitter
- identical experimental conditions
- Scan time reduced by factor 2

K. Iwaszczuk *et al.*, Opt. Express **17,** 21969 (2009)